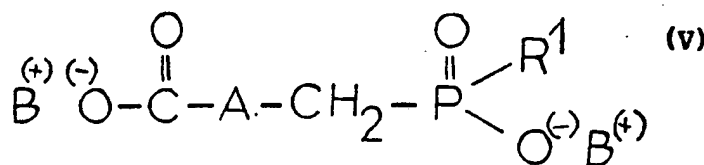
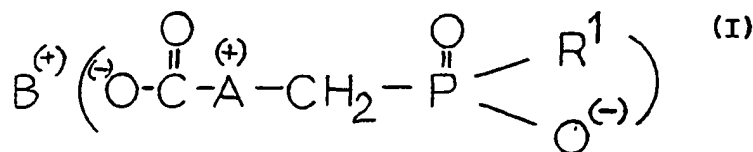




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(71) Applicant: ALKALOIDA VEGYÉSZETI GYÁR RT. [HU/HU]; Kabay J. u. 29, H-4440 Tiszavasvári (HU).			
(72) Inventors: POWELL, Fulgencio ; Kelp I u. 3, H-4440 Tiszavasvári (HU). LITKEI, László ; GALAMB, Vilmos ; Elmunkás u. 2, H-4440 Tiszavasvári (HU). GULYÁS, Imre ; Ifjúság u. 4/4, H-4440 Tiszavasvári (HU). RÉPÁSI, János ; RÉPÁSINÉ VERES, Ágota ; Ifjúság u. 1/4, H-4440 Tiszavasvári (HU). VIGH, József ; Kabay J. u. 17, H-4440 Tiszavasvári (HU). KOCZKA, Istvánné ; Zrínyi u. 15, H-4440 Tiszavasvári (HU). FEHÉRVÁRI, Edit ; Wesselényi u. 11, H-4440 Tiszavasvári (HU). RÓKA, Lászlóné ; Gergely D. u. 13, H-4440 Tiszavasvári (HU). PETHE, Lászlóné ; Vass G. u. 19, H-4440 Tiszavasvári (HU). NEU, József ; Kelp I. u. 1/a, H-4440 Tiszavasvári (HU).		Published <i>With international search report.</i>	

(54) Title: **NEW NON-HYGROSCOPIC MONO-AMMONIUM SALTS**

(57) Abstract

New, non-hygroscopic, crystalline mono-ammonium salts of general formula (I), where, R¹ stands for hydroxy or alkyl; -A stands for 1-4 alkyl-amino- or amino-alkyl-groups containing primary or secondary amino-groups, preferably -CH₂-NH- or -CH(NH₂)-CH₂-groups; B stands for ammonium, -ion, or alkyl-substituted ammonium-ion- as well as processes to obtain the same by preparing the mono-ammonium salt of general formula (I), according to any method known generally for the preparation of salts, whereby, along with avoiding other contaminations, on the course of or after salt-formation the di-ammonium salt of general formula (V), where, -R¹, A and B stand for the above, is eliminated or its formation is repressed. Herbicidal or plant-growth-regulating compositions containing the non-hygroscopic salts, processes for their preparation and methods of treatment of unwanted plants and weed as well as a composition consisting of a bag, which is solid and preferably flexible in its dry state, which is made of a water-soluble polymer and which contains the new substances or compositions.

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NEW NON-HYGROSCOPIC MONO-AMMONIUM SALTS.

The invention relates to new mono-ammonium salts, their preparation and use as active ingredients of pesticides.

More particularly the invention relates to new solid, non-hygroscopic mono-ammonium salts of general formula I which are substantially free of diammonium-salts of the general formula V, processes for their preparation, pesticide compositions containing the same, as well as preparation and use of said pesticide compositions.

In this specification the meaning of the substituents in the general formulae is always the following:

- R¹ stands for hydroxy or alkyl-groups,
- A stands for 1-4 alkyl-amino- or amino-alkyl-groups containing primary or secondary amino-groups, preferably -CH₂-NH- or CH(NH₂)-CH-groups,
- B stands for ammonium-ion, or alkyl-substituted ammonium-ion,
- R² stands for hydrogen, hydroxyl-, optionally substituted 1-4 alkyl-groups, optionally substituted aryl-group.

The salts of general formula I are known as active ingredients of pesticides and their preparation and properties have been described in literature. The mono-ammonium salts of general formula I however are never described to appear in other form than as hygroscopic products, which are not resistant against humidity of normal atmosphere so that their application as pesticides was therefore only brought about by dissolving the products in water and selling the product in aqueous solutions.

The inconvenience of this procedure is clear. It was therefore the aim of our invention to find a method whereby the mono-ammonium salts of general formula I - especially the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine and the mono-isopropylammonium salt of (3-amino-3-

WO 92/18513

carboxy-propyl)-methane phosphinic acid can be obtained in a form which is non-hygroscopic, enabling thus the transportation, commercialisation and even the use in solid form, or - when direct use on the field is brought about in aqueous solution - to ensure that the solid can be dissolved before use, bringing thus transportation and storage to reasonable costs as compared with the present situation when aqueous solutions are transported and stored. The aqueous solutions in commerce contain 30 - 50% of the active ingredient as a maximum. Handling of the hygroscopic salts also causes environmental and health-care problems which would be avoided with non-sticky, non-hygroscopic products. The products have mostly acidic character and attack even the material in which they are transported so that greatest care and the proper material for their protection is needed - which all increase the costs of application.

The most important representatives of the compounds of general formula I are the pesticide ingredients mono-isopropylammonium salt of N-(phosphonomethyl)-glycine and the mono-isopropylammonium salt of (3-amino-3-carboxy-propyl)-methane phosphinic acid- however their ammonium-salts are also important.

The above salts, their preparation and use was described in several publications such as USP 3.315.675, 3.56.672, 4.405.531, 3.868.407, 4.140.513, 4.315.765, 4.397.676 and HU-Patent 184.601 as well as USP 3.288.846, 4.507.250, 4.147.719, 4.487.724, German Patent 3.312.165, European Patents 249.188, 265.412, 301.391, and Japanese Patents 60.248.190, 02.190.196, 59.181.288.

Different methods were developed to avoid the consequences mentioned above. Thus different additives were proposed as auxiliary agents to ensure the production of wettable powders and their use /e.g. European Patents 256.942, 352.508, Japanese Patents 01.42.409, 58.18.311, 62.175.407, 62.175.408, and USP 4.405.531. However when used in practice great care has to be taken to protect these

powders against humidity, to use up the bags when opened, to store the products under proper conditions etc. - whereby the additional materials do not give the results that are aimed at when used for some time. Another approach of the problem was the suggestion to spray-dry the product /Jap.Pat. 63.10.701/ or again a different one to admix the salt with a solvent and a moulded surface active agent - giving thus a mixture from which the solvent is evaporated and the surface active agent is cooled until solidified, whereupon the solid product is formulated /European Patent 02.06.537/.

The preparation of the salts is mostly brought about by reacting the acidic partner with the basic partner reactant in aqueous media, (e.g. Hungarian Patent 185.003, Swiss Patent 620.812 and German Patent 2.717.440) though the literature also teaches reaction of the acid with the basic reactant without solvents, whereupon the a mould of surface active agent is added to the reaction mixture and formulation is carried out after cooling of the mixture. /See also Spanish Patent 530.743 where benzene or water are proposed as solvents for a similar method./

All publications are common - when making any statement about the quality of the products obtained - that they are hygroscopic /e.g. German Patent No.2.717.440, Swiss Patent No.620.812 for the ammonium salt of glufosinate/ and some state that the products are solidified as glassy materials which can be ground in mortars but still are hygroscopic when stored.

According to Hung. Pat. Appl. 1322/90 a new formulation of N-(phosphonomethyl)-glycine comprises a water-soluble bag containing the sodium or the potassium salt of N-(phosphonomethyl)-glycine as a wettable powder, which is easy to use. The authors of said patent teach, that they were unable to make similar formulations using the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine because of the extreme hygroscopic nature of the mono-isopropylammonium salt. Nor is the aqueous solution of the

WO 92/18513

PCT/HU92/00016

mono-isopropylammonium salt of N-(phosphonomethyl)-glycine suitable (according to said publication) because the solution dissolves the material of the bag before use.

When investigating some of the products obtained according to some of the known methods /e.g. when reproducing the processes of European Patent 02.56.608 and Spanish Patent 530.743/ we found that these mono-isopropylammonium salts always contained certain amounts of di-ammonium-salts of general formula V together with acids of general formula II.

The presence of small amounts of the di-ammonium-salts of the general formula V is not evident from the analysis data of the products obtained by way of classical analysis methods: the content of free acids of general formula II together with the content of di-ammonium-salts of general formula V might give analytical data as a total result which hide the presence of the di-ammonium salts in the products.

When isolating di-ammonium-salts of general formula V we ascertained that these salts differ considerably from the mono-ammonium salts as regards hygroscopicity so that slight amounts of the di-ammonium-salts influence the hygroscopic properties of such salts dramatically.

When investigating the N-(phosphonomethyl)-glycine obtained with known methods by means of FT - IR spectroscopy we found that the products always contained the carbonyl valency oscillation bonds of free N-(phosphonomethyl)-glycine at 1717 and 1733 cm^{-1} wave length and the carboxylate oscillations of the free carboxylate in the N-(phosphonomethyl)-glycine di-isopropylammonium-salt at 1561 and 1633 cm^{-1} . The change of the proportions of these bonds shows the change in the ratio of components. This was shown by preparing standard samples of the mono - and the

di-iso-propyl-ammonium salts and taking their calibration spectra.

It can be seen from the IR spectroscopic data that also glufosinate exists in two different forms of twin-ionic structure. Thus the carboxyl group can appear both in dissociated form at 1640 and 1600 cm^{-1} and in non-dissociated form at the absorption band at 1733 cm^{-1} and 1728.

Care has to be taken when preparing the samples as well. Sometimes the mono-ammonium-salts - which are contaminated with di-ammonium-salts as well as with the free acid - are subject to additional reaction steps when the samples are dissolved before taking the spectra - giving thus results that are not typical for the product before measurement.

When comparing the spectra obtained with our own methods it is clear that in the products prepared according to our invention the un-dissociated carbonyl group absorption bonds disappear at 1730 cm^{-1} and the dissociated carboxyl bonds which are characteristic for the salts increase at 1640 and 1600 cm^{-1} .

When already having the above spectroscopic data the HPLC methods and automatic melting point analytical methods can be used to complete definition of the properties of the new salts.

"Non-hygroscopic" according to our invention means, that when exposed at 25°C to an environment containing 60% humidity no observable uptake of water takes place within 3 weeks or this uptake is less than 0.1%. The salts are crystalline, they have melting point ranges that are different from those published before and their water-solubility is somewhat increased as compared with the salts prepared with the known methods.

First objects of our invention are thus non-hygroscopic salts of general formula I.

Preferred products according to our invention are the solid, non-hygroscopic mono-isopropylammonium salts of N-(phosphonomethyl)-glycine of the α and/or β crystal type.

The α -crystal-type has a melting point range of 158 - 163°C and the characteristic values of crystal - lattice - levels when measured by way of X-ray-diffraction are as follows: 11.0, 9.06, 5.94, 5.54, 4.13, 3.71, while the characteristic absorption bands obtained by FT-IR-spectroscopy are 1660, 1600, 1553, 1545, 1075, 513 and 475 cm⁻¹.

Other preferred products according to our invention are the solid, non-hygroscopic, crystalline mono-isopropylammonium salts of N-(phosphonomethyl)-glycine of the β crystal type, having a melting point range of 143 - 154°C and the characteristic values of crystal - lattice - planes when measured by way of X-ray-diffraction are as follows: 7.00, 4.47, 3.35, 2.815, while the characteristic absorption bands obtained by FT-IR-spectroscopy are 1645, 1594, 1561, 1541, 1066, 500 and 455 cm⁻¹.

The mono-isopropylammonium salt of N-(phosphonomethyl)-glycine can thus appear in two different crystal types which we named α and β types. None of these has ever been described as a non-hygroscopic, crystalline product.

A further preferred product according to our invention is the solid, non-hygroscopic, crystalline (3-amino-3-carboxypropyl)-methane-phosphinic acid mono-isopropylammonium salt having a melting point range of 199 - 203°C, while the characteristic absorption bands obtained by FT-IR-spectroscopy are 1640, 1601, 1530, 1138, 1037, 750 and 471 cm⁻¹.

A further subject of our invention is the process for the synthesizing of a solid, non-hygroscopic salt by preparing the mono-ammonium-salt of general formula (I) according to a method known generally for the preparation of salts, whereby - along with avoiding other contaminations - on the

course of or after salt-formation the di-ammonium-salt of the general formula (V) is eliminated or its formation is repressed.

Preferred processes according to our invention comprise the use of the following processes alone or in combination with each other

a.)

reacting the acid of the general formula (II) with a reactant of basic (alkaline) character capable to form the ion B^+ -in an organic, polar solvent or in solvent- mixture containing an organic, polar solvent, in which the salt and acid of general formulae (I) and (II) are not, or only slightly soluble, while the reactant of basic character and the di-ammonium-salt of general formula (V) formed as by-product are readily soluble, and optionally the reaction mixture is heated subsequently or

b.)

a di-ammonium-salt of the general formula (V), is reacted with an acid of the general formula (II) under the reaction conditions of the method a) or

c.)

an acid of the general formula (II) is reacted with a salt capable to form the ion B^+ under the reaction conditions of the method a) or

d.)

a hygroscopic salt of the general formula (I) is extracted with an organic, preferably polar solvent or a solvent-mixture containing an organic, polar solvent, in which the mono-ammonium salt of general formula (I) is insoluble or slightly soluble, while the di-ammonium-salt of general formula (V) is readily soluble or

e.)

eliminating at room temperature in vacuo or with heating from a di-ammonium salt of general formula (V) or from a

mono-ammonium salt which is contaminated with such di-ammonium-salt the quantity of the amine containing the B^+ -ion which is above the mole-equivalent, or

f.)

reacting a salt of the acid of the general formula (II), using the reaction conditions of the a.) method with a reactant which is capable to form the ion B^+ - and optionally isolating the salt of general formula (I) thus formed preferably by filtration.

When carrying out the above processes it is preferable to use as a starting acid N-(phosphonomethyl)-glycine of formula (III), or (3-amino-3-carboxy-propyl)-methane-phosphinic acid of the formula (IV).

Solvents that are suitable for our process are aliphatic alcohols containing 1-6 carbon atoms and/or poly-alcohols and/or aromatic alcohols containing 1-6 alkyl side chains. It is preferable to prepare N-(phosphonomethyl)-glycine - mono-isopropyl-ammonium-salt or - mono-ammonium-salt in the presence of ethanol and/or propanol. Preferred temperature ranges for the method c.) reactions are 0 - 150°C, preferably 20 - 80°C.

According to method a.) it is essential to use the proper solvents that have to be chosen according to our invention. As stated above, it is the solubility tests that have to be performed before such choice is made. It is essential that such solvents have to be used in which the salt of general formula (I) and the acid of general formula (II) are practically insoluble or but slightly soluble, while the reactant of alkaline character and the di-ammonium-salts of general formula (V) are readily soluble.

A supposition of how the process might take its course is the following: The reaction starts on the surface of the acid particles suspended in the solvent system. Since the acid is two-basic and the amines are present in excess, on the surface of the acid the di-ammonium salts are formed,

which - because they are readily soluble in the solvent - quit the surface of the acid particles and dissolve, leaving the surface open to enter into reaction with further amounts of amine. As soon as the amine or other basic reactant is used up, the remaining dispersed acid and the di-ammonium-salt in solution can enter into an ion-transfer reaction so that the mono-ammonium salt is formed. Since the solubility of the mono-ammonium-salt is very small in the solvent-mixture used, the mono-ammonium salt precipitates continuously.

We have found that polar organic solvents or such solvent mixtures which contain organic polar solvents are suitable for the purpose of method a.) of our invention.

The above theory is supported with the changes which can be observed when e.g. N-(phosphonomethyl)-glycine is reacted with isopropylamine according to method a.) of our invention:

When a dispersion of the N-(phosphonomethyl)-glycine in absolute ethanol is made a liquid of strong white colour is obtained. On subsequent addition of isopropylamine the colour gets lighter and - on addition of the whole quantity of isopropyl amine and eventually after heating - the reaction mixture gets clear, almost transparent, followed by precipitation of the mono-ammonium-salt on cooling.

Once knowing that the above method is suitable for the preparation of the mono-ammonium-salt which is substantially free of the di-ammonium salt, the application of other methods is also possible.

To investigate the process we prepared the di-ammonium-salt using double amounts of the isopropylamine and made tests concerning this product and its solubility. /see Tables IV and V. We then used this products as starting materials for methods b.) and e.) of our process.

The above experiments also show why it was not possible to

obtain pure mono-ammonium-salts according to the methods of EP 256 608 and Spanish Patent 530 743: They used solvents in which the di-isoproylammonium salt is not readily soluble and resulting in considerable contamination of the mono-ammonium-salt with both the di-ammonium-salt and the starting acid.

When using the method c.) it is advantageous to react the acid of general formula (II) with the salt formed with a 1 or 2 basic carboxylic acid of the pK-value of the range 2,27 to 5,8. The acids may have the general formula (VI).

Thus when preparing alkyl-ammonium salts according to the method c.) one may proceed by applying the alkyl-ammonium salt of the acid of the general formula (VI) which is added to the reaction in solid form or in solution.

Preferred temperature ranges for the method c.) reactions are 0 - 150 °C, preferably 20 - 80 °C.

According to our method c.) the salts of the amines are used. The salts are generally easier to handle than the amines, which have rather low boiling points. Preferable carboxylic acids are for example such as acrylic acid, benzoic acid, acetic acid, formic acid, propionic acid, butyric acid, valeric acid and others.

The salts may be prepared separately and the isolated salts may be added to the acids of general formula II. However one may also proceed by preparing the salt in solution, and add the solution without isolating the salt after making the proper analytical evaluations.

The processes according to our invention are simple, they do not need any special equipment, they do not raise environmental problems while leading to the new crystalline mono-ammonium salts according to our invention.

A further object of our invention are herbicidal or plant-growth-regulating compositions containing as an active ingredient an effective amount of the crystalline, non-hygroscopic salts of the general formula (I).

Especially important are those herbicidal or plant-growth-regulating compositions according to our invention which contain as an active ingredient an effective amount of a crystalline, non-hygroscopic (3-amino-3-carboxy-propyl) - methane-phosphinic acid mono-isopropyl - ammonium salt or of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine of the α and/or β crystal type.

Preferred compositions according to our invention include compositions containing as an active ingredient 0.1 to 99.9% of the above salts along with additive and auxiliary products which are used in pesticide industry and/or products which favorably modify the properties of the composition when applied for agricultural use.

As additive and auxiliary products surface active agents reducing surface tension may be used which may be cationic, anionic, non-ionic or amphoteric as well. Further additives include adjuvants, adhesion promoting and decreasing substances, inhibitors of dust and foam formation, promoters of dissolution, solid or liquid vehicle substances, dispersing, colouring agents, products that increase resistance against rain or corrosion, activators and the like.

Preferable auxiliary products are the following:

- water-soluble alkyl-sulphates, alkyl-phosphates,
- alkyl-benzene-sulphonate,
- naphthyl-sulphonates, alkyl-naphthyl-sulphonates,
- sulphatized fatty alcohols, amines, acid amides,
- sulphatized, or sulphonated fatty acid esters,
- sulphonated plant oils,
- alkyl-phenols such as iso-octyl-phenol and nonyl-phenol
- polyoxy-ethylene derivatives and hexythal anhydrides

WO 92/18513

PCT/HU92/00016

- poly (oxy-ethylene) derivatives of mono-(long carbon chain) fatty acid esters
- polyoxy-ethylene-alkyl-ether, polyoxy-ethylene-alkyl-aryl-ethers,
- polyoxy-ethylene-alkyl-aryl-ether formaldehyde condensates,
- polyoxy-ethylene-alkylene-aryl-ethers,
- polyoxy-alkylene-alkyl esters,
- polyoxy-alkylene-sorbitol-, sorbitane and glycerol esters,
- polyoxy-alkylene block copolymers,
- polyoxy-alkylene-allyl-sulphonamides,
- polyoxy-alkylene-alkyl-glycerol-esters,
- polyoxy-alkylene-resin esters,
- polyoxy-propylene block copolymers,
- polyoxy-ethylene-oleyl ethers,
- polyoxy-alkylene-alkyl-phenols and mixtures thereof
- polyoxy-alkylene-alkyl-amines such as ethoxylated tallow-amine, ethoxylated olein-amine,
- ethoxylated soy amine, ethoxylated cocoa amine, ethoxylated
- synthetic alkyl-amines, propoxylated amines and mixtures
- polyoxy-alkylene-alkyl and alkyl-aryl-ether-sulphates,
- polyoxy-alkylene styryl-phenyl-ether-sulphates,
- alkyl-naphthalene-formaldehyde condensates,
- alkyl-diphenyl-ether-sulphonates,
- poly-oxy-alkyn-alkyl-phosphates
- polyoxy-alkylene-phenyl-ether-phosphates,
- polyoxy-alkyl-phenol-phosphates,
- polycarboxylates, N-methyl-fatty acid laurides,
- amine-oxydes, such as lauryl-dimethyl-amine-oxyde,
- surface active salts of N-(phosphono-methyl)-glycine e.g. N-(phosphono-methyl-glycine N,N-bis(hydroxy-ethyl-cocusamine salt
- saturated fatty alcohols,
- organic acid esters, lactic acid ethyl ester, dibutyl-phthalate, adipic acid-isopropylester,
- fatty acids, fatty acid salts, fatty acid esters,
- ethyl-oleate, ethyl-stearate, di-n-butyl-adipate,
- lauric acid-hexylester, dipropylene glycole-pelargonate,
- isopropyl-myristate, isopropyl-palmitate, isopropyl-stearate,
- oleic acid, oleyl-ester, oleic acid-dodecyl-ester, polyglyceryl-lauric acid ester,
- capryl/capric acid esters of saturated fatty alcohols,

- glycerol-poly-vinyl-alcohol derivates,
- phospholipides, alkyl-polyglycoside derivates
- methyl-, hidroxy-ethyl-, hydroxy-methyl and other cellulose-
se derivates
- poly-vinyl derivates,
- lignine sulphonates, polymeric alkyl-naphthaline sulphonates,
- poly-(methylene)-bis- (naphthalene sulphonate), N-methyl-N-(long chain) fatty acid laurates
- quaternary ammonium salts, alkyl-, and alkyl-aryl ammonium halogenides, e.g. 10-18 carbon atom alkyl-dimethyl-, alkyl-trimethyl-, alkyl-benzyl-dimethyl-ammonium-chlorides e.g. cetyl-trimethyl-ammonium chloride,
- anionic, cationic, non-ionic, or amphoteric flour- aliphatic wetting agents,
- silicone-copolimer-based surface activants,
- tetraethoxy-silane derivates,

The compositions may preferably contain special, inorganic or organic nitrogen containing products as additives, such as urea, urea - derivatives or further inorganic salts such as calcium-, sodium-, ammonium- chloride, - sulphate, -phosphate, - borate and the like.

They also may contain paraffine hydrocarbons, mineral oil fractions, natural plant oils, organic solvents.

Inert vehicle products such as diatomaceous earth, caoline, attapulgit, fuller earth, montmorillonit, bentonite, synthetic silicic acids, thiosulphates and other agents which are adjuvants when using the compositions.

Being solid products the compositions may take different forms depending of the requirements of use such as pellets, powders, tablets, granules using suitable equipments.

In addition to the above the compositions according to the invention may also include further products which have pesticide or other biological activity per se. These might be insecticides, fungicides herbicides, plant growth

WO 92/18513

PCT/HU92/00016

regulating agents or chemical fertilizers, trace elements etc.

Preferable combination partners of this type are e.g. the following:

2,4-D = 2,4-dichloro-phenoxy-acetic acid
endotal = 7-oxobicyclo/2,21/heptene-2,3-dicarboxylic acid
2,4,5-T = 2,4,5-trichloro-phenoxy-acetic-acid,
MCPA = 4-chloro-o-tolyloxy-acetic acid,
MCPB = 4-(4-chloro-o-tolyloxy)-acetic acid,
glufosinate = ammonium-/3-amino-3-carboxy-propyl/-methyl-phosphinate,
bialafos = dl-homoalanine-4-yl-methyl-phosphinate
ethephon = 2-chloro-ethane-phosphonic acid,
mekoprop = 2-/2-methyl-4-chloro-phenoxy-propionic acid,
pikloram = 4-amino-3,5,6-trichloro-picolinic acid,
benzak = 2,3,6-trichloro-benzoic acid,
dalapon = 2,2-dichloro-propionic acid,
dikamba = 3,6-dichloro-o-anis acid,
dichlorprop = 2-/2,4-dichloro-phenoxy/-propionic acid
scepter = 2-/4,5-dihydro-4-methyl-4-/1-methyl-ethyl/-5-oxo-1H-imidazole-2-yl-3-quinoline carboxylic acid
pursuit = 2-[4,5-dihydro-4-methyl-4-/1-methyl-ethyl/-5-oxo-1H-imidazole-2-yl]-5-ethyl-3-pyridine carboxylic acid,
atrazin = 2-chloro-4-/ethyl-amino/-6-/isopropylamino/-s-triazine
simazin = 2-chlor-4,6-bis/ethyl-amino/-s-triazine,
diuran = 3-/3,4-dichloro-phenyl/-1,2-dimethyl-urea,
linuron = 3-/3,4-dichloro-phenyl/-1-methoxy-1-methyl-urea,
NES = 1-naphthyl acetic acid,
orest = 2-[3-(4,6-dimethyl-pyrimidine-2-yl)ureido-sulphonyl]-benzoic acid,
glean = 1-[2-chloro-phenyl-sulphonyl/-3-/4-methoxy-6-methyl-1,3,5-triazine-2-yl]-urea,
allin = methyl-2-[(4-methoxy-4-methyl-1,3,5-triazine-2-yl)-amino-carbonyl]-amino-sulphonyl-benzoate,
klasszik = ethyl-2-[(4-chloro-6-methoxy-pyrimidine-2-yl)-amino]-carbonyl-amino-sulphonyl-benzoate
fomesafen = 5-[chloro-4-(trifluoro-methyl)-phenoxy]-N-methyl-

sulphonyl/-2-nitrobenzamide,
-oxyflurofen = [2-chloro-1-(3-ethoxy-4-nitro-phenoxy)-4-
/trifluoro-methyl]-benzene,
-feroe = [phenoxaprop-ethyl(+_)ethyl-2,4(-6-chloro-2-
benzoxazolyl)-oxy-phenoxy]-propanoate,
-alachlor = 2-chloro-2,6,,,-diethyl-N-/methoxy-methyl/-
acetanilide,
-propachlor = N-isopropyl-2-chloro-acetanilide,
-butachlor = N-/butoxy-methyl/-2,6-diethyl-2-chloro-
acetanilide,
-metachlor = 2-chloro-2-ethyl-6-methyl-N-/1-methyl-2-methoxy-
ethyl/-acetanilide etc.

A further object of our invention consists in processes for the preparation of a herbicidal or plant - growth regulating compositions by formulating with the methods known for formulating of pesticides 0.1 to 99.9% of an active ingredient according to our invention together with auxiliary products used in pesticide formulation and/or with products which favorably modify the properties of the active ingredients when used including products that have biological properties or are known to be active ingredients of pesticides per se.

Further objects of our invention are herbicidal or plant-growth-regulating compositions consisting of a bag, which is solid in its dry state, which is made of a water-soluble polymer and which contains the compositions according to our invention.

Preferred products of this type are those containing the mono-isopropylammonium salt or mono-ammonium-salt of N-(phosphonomethyl)-glycine or the mono-isopropylammonium salt or mono-ammonium-salt of glufosinate.

The bags used according to the invention are of the size taking 0.1 - 10 kg, preferably 0.5 - 5 kg of the compositions according to the invention. They may preferably be totally filled with the composition of the inven-

tion. However some space might be left to facilitate addition of certain substances before use.

The bags are solid and flexible at the temperature and humidity of the ambience. The thickness of the walls amounts to 20 - 100 microns, preferably to 30 - 60 microns and they are welded at at least one side.

The water-soluble bags used according to our invention as above are known per se. The water-soluble polymer applied may be the following:

- polyvinyl alcohol polymers, especially polyvinyl alcohol polymers plastified with polyvalent alcohols,
- methyl cellulose
- ethylene oxyde copolymers
- polymers of vinyl pyrrolidone or vinyl acetate,
- gelatine, carboxy methyl cellulose, dextrose, hydroxyethyl-cellulose or
- methyl cellulose combined with polyvalent alcohols, such as ethylene glycol, propylene glycol, glycerol, sorbitol and others.

It might be necessary to protect the bags by putting them into bigger containers or collective packages. These may be made of cheap material such as plastics, cardboard or aluminium. These do not influence safety of the products for the environment because they do not contact the pesticid within the polymer bags according to our invention directly.

The polymer bags according to our invention may contain the mono-ammonium salt of general formula I alone or in form of the compositions as detailed above. They may also contain additional products such as protecting colloids, products to increase density, tyxotropic products, stabilizers etc.

When using the bags according to our invention the bags are thrown into the required amount of water while stirring intensively. The polymer material disappears within about 2 minutes, the herbicide composition dissolves or disperses

in the water and the liquid thus obtained can be used in the field as needed.

A further object of the invention consists in a method to kill unwanted plants or to influence the growth of plants by treating said plants in the field with an effective amount of a herbicidal or plant-growth-regulating composition according to our invention by way of dispersing the composition on the plants in the form of aqueous or water / organic solvent solutions or dispersions or suspensions.

Figures 1 to 6 show the following:

Figure 1 : X-ray diffraction spectrum of N-(phosphonomethyl)-glycine mono-isopropylammonium salt α crystal type. Intensity against angle.

Figure 2 : X-ray diffraction spectrum of N-(phosphonomethyl)-glycine mono-isopropylammonium salt β crystal type. Intensity against angle.

Figure 3 : DSC examination of N-(phosphonomethyl)-glycine mono-isopropylammonium salt α type crystals. Heat flow W/g against temperature °C.

Figure 4 : DSC examination of N-(phosphonomethyl)-glycine mono-isopropylammonium salt β type crystals. Heat flow W/g against temperature °C.

Figure 5 : DSC examination of N-(phosphonomethyl)-glycine mono-isopropylammonium salt α type and β type crystals in a mixture of 1:1. Heat flow W/g against temperature °C.

Figure 6 : FT-IR spectrum of N-(phosphonomethyl)-glycine mono-isopropylammonium salt α type crystals. Absorbance against wave numbers.

WO 92/18513

Details of the invention are given in the Examples by way of illustration and not of limitation.

I. CHEMICAL EXAMPLES

Example I.1.

50 g (0.3 moles) of N-(phosphonomethyl)-glycine are reacted with 17.5 g (0.3 moles) of isopropylamine in 200 ml of 96% ethanol at room temperature. The mixture is refluxed for half an hour, filtered, concentrated by evaporation and crystallized. 69g (0.3 moles) of crystalline, dried mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. The product is not hygroscopic, readily soluble in water. Melting range 161 - 163°C. It contains 73.9% N-(phosphonomethyl)-glycine. Yield 99.95%. Characteristic absorption bands (FT-IR spectroscopy, cm^{-1}) 1660, 1600, 1553, 1545, 1075, 513, 475, characteristic values of crystal-lattice-planes measured with X-ray diffraction: 11.0, 9.06, 5.94, 5.54, 4.13, 3.71. (α type crystals).

Example I.2.

100g (0.59 moles) of N-(phosphonomethyl)-glycine are reacted with 35g (0.59 moles) of isopropylamine in 400 ml of absolute ethanol at room temperature. The suspension warms up to 49°C and is then refluxed for half an hour by heating to 78°C. On cooling to room temperature, filtration and drying 129.0 g (0.57 moles) of crystalline mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. The product is not hygroscopic, readily soluble in water. Mp: 161 - 162°C. It contains 74% N-(phosphonomethyl)-glycine. Yield: 99.86%. Characteristic absorption bands /FT-IR spectroscopy, cm^{-1}): 1660, 1600, 1553, 1545, 1075, 513, 475, characteristic values of crystal-lattice-planes measured with X-ray diffraction: 11.0, 9.06, 5.94, 5.54, 4.13, 3.71. (α type crystals)

Using the method of Example I.2. the following results are obtained :

WO 92/18513

PCT/HU92/00016

Ex.	amine	solvent	pmg*-salt g/mp °C	yield %	pmg con- tent %
I.3.	iso- propyl-	n.propanol	130.7g 159-160	99.9	74
I.4.	iso- propyl	n.butanol	129.33g 159-160	99.91	74
I.5	iso- propyl	n.amyl- alcohol	123.7g 158-159	98.7	73.2
I.6.	iso- propyl	dimethyl- formamide	115.1g 148-153?	98	73.0

*=N-(phosphonomethyl)-glycine

Example I.7.

200 g (1.18 moles) of N-(phosphonomethyl)-glycine and 140 g (2.37 moles) of isopropylamine are reacted in 600 ml of ethanol and the reaction mixture which warms up to 58°C by reaction heat is further refluxed for half an hour. On cooling, evaporation and filtration 335.8 g (1.17 moles) of the di-(mono-isopropylamine)-salt of N-(phosphonomethyl)-glycine are obtained in the form of light crystals. The product is readily soluble in water, mp. 145 - 150°C. N-(phosphonomethyl)-glycine content: 57.5%

170 g (0.59 moles) of N-(phosphonomethyl)-glycine-di-(mono-isopropylamine)- salt are reacted with 100 g (0.59 moles) of N-(phosphonomethyl)-glycine in 400 ml of ethanol, refluxed for half an hour and the milk-like suspension is filtered on cooling to room temperature. The product obtained is dried to give 269.2 g (1.18 moles) of mono-isopropylammonium salt of N-(phosphonomethyl)-glycine, melting at 158 - 160°C. The product is non-hygroscopic and contains 74% of N-(phosphonomethyl)-glycine.

Example I.8

100 kg of N-(phosphonomethyl)-glycine are added to 400 l of ethanol in an autoclave vessel of 1 m³. 35 kg of isopropylamine are added under nitrogen atmosphere to the mixture of 20°C while stirring constantly. The mixture warms up to

45°C and is then heated to its boiling point and refluxed for 1 hour. On cooling to 20°C the mono-isopropylammonium-salt of N-(phosphonomethyl)-glycine is centrifugated, the salt washed with 30 l of ethanol and dried after repeated centrifugation. The washing is united with the mother layer.

130.1 kg of mono-isopropylammoniumsalt of N-(phosphonomethyl)-glycine are obtained. Contains 74% of N-(phosphonomethyl)-glycine. The product is non-hygroscopic, readily soluble in water. Mp: 153 - 156°C.

Example I.9

181 g (1 mole) of (3-amino-3-carboxy-propyl)-methane-phosphinic acid are reacted with 59g (1.0 mole) of isopropylamine at room temperature in 300 ml of methanol. The mixture is refluxed at 65°C for 30 minutes, cooled, filtered and the crystals are dried to give 232g of mono-isopropylammoniumsalt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid, which is non-hygroscopic, readily soluble in water, melting at 203 - 203.5°C, containing 75% (3-amino-3-carboxy-propyl)-methane-phosphinic acid. Yield: 97%

Example I.10

181 g (1 mole) of (3-amino-3-carboxy-propyl)-methane-phosphinic acid are reacted with 59g (1.0 mole) of isopropylamine at room temperature in 800 ml of ethanol. The mixture is refluxed for 30 minutes, cooled, filtered and the crystals are dried to give 2352g of mono-isopropylammoniumsalt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid, which is non-hygroscopic, readily soluble in water, melting at 199 - 203°C, containing 74% (3-amino-3-carboxy-propyl)-methane-phosphinic acid. Yield: 98%.

Example I.11

181 g (1 mole) of (3-amino-3-carboxy-propyl)-methane-phosphinic acid are reacted at room temperature with 17g (1.0 mole) of ammonia (previously dissolved at 0°C in methanol). The mixture warms up spontaneously to 35°C and is then refluxed at 65°C

for 30 minutes, cooled, filtered and the crystals are dried to give 193g of (3-amino-3-carboxy-propyl)-methane-phosphinic acid ammonium salt, which is non-hygroscopic, readily soluble in water, melting at 207 - 209°C, containing 90% of (3-amino-3-carboxy-propyl)-methane-phosphinic acid. Yield: 97.5%

Example I.12

169.1 g (1mole) of 100% N-(phosphonomethyl)-glycine and 59.11g (1 mole) of 100% pure i.propylamine are reacted in 700 ml of absolute ethanol at room temperature. The suspension is refluxed for 30 minutes, cooled to room temperature and filtered. 216.78g (0.95 moles) of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. The product is crystalline, non-hygroscopic, readily soluble in water, melting at 161 - 163°C. Characteristic absorption bands /FT-IR spectroscopy, cm^{-1}): 1660, 1600, 1553, 1545, 1075, 513, 475, characteristic values of crystal-lattice-planes measured with X-ray diffraction: 11.0, 9.06, 5.94, 5.54, 4.13, 3.71. α -type crystals Fig. 1, 3, 6)

Example I.13

The reactants as in Example I.12 are reacted in 70 ml of distilled water, while the i.propylamine is added slowly. The solution obtained is heated for 1 hour at 100°C, cooled to room temperature, the crystals filtered and dried. 228.20 g (1 mole) of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. The product is non-hygroscopic, readily soluble in water, melting range 147 - 153°C. β type crystals, see Fig 2, 4.

Example I.14

The product obtained according to Example I.12 is refluxed for 2x0.5 hours in 700 ml of absolute ethanol while heating, cooled at room temperature, filtered and dried. 220g of mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. The product is non-hygroscopic, readily soluble in water, melting range 148 - 154°C. (β type crystals)

Example I.15

16.9g (0.1 mole) of N-(phosphonomethyl)-glycine are stirred in 40 ml of water-free ethanol and 11.9g (0.1 mole) of isopropylamine acetate are added, followed by heating to 80°C for 30 minutes. On cooling to room temperature the crystals are filtered, washed with ethanol and dried. The crystalline mono-isopropylammonium salt of N-(phosphonomethyl)-glycine is non-hygroscopic, readily soluble in water, melting range 154 - 157°C. (β type crystals). Yield 96.6%. It contains 73.8% of N-(phosphonomethyl)-glycine.

Example I.16

The process of Example 44 is repeated with the difference, that 14.87g (0.125 moles) of isopropylamine acetate are used. 21.6g of crystalline mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. The product is non-hygroscopic, readily soluble in water, melting range 153 - 157°C. (β type). Yield 95%. It contains 74.1% of N-(phosphonomethyl)-glycine.

Example I.17

16.9g of N-(phosphonomethyl)-glycine are stirred in 20 ml of water and 11.9g of isopropylamine acetate are added. The solution gets clear after a while and is then poured on a watch-glass. After evaporation of the water at room temperature while standing 22.8g of crystalline mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. The product is non-hygroscopic, readily soluble in water, melting range 148 - 156°C. (β type). It contains 74.1% of N-(phosphonomethyl)-glycine.

Example I.18

16.9g of N-(phosphonomethyl)-glycine are stirred in 30 ml of methanol and 9.1 g of dimethylamine-formiate are added. On working up as in the above examples 21.31g of crystalline mono-(dimethyl-ammonium)-salt of N-(phosphonomethyl)-glycine are obtained. The product is non-hygroscopic, readily soluble in water, melting range 118 - 124°C. It contains 78.3% of N-(phosphonomethyl)-glycine.

Example I.19

16.9g of N-(phosphonomethyl)-glycine are reacted as in Example I.18 with 11.9 g of ethylamine-propionate in 30 ml of isopropanol. 19.9 g of crystalline mono-ethylammonium salt of N-(phosphonomethyl)-glycine are obtained. The product is non-hygroscopic, readily soluble in water, melting range 131- 137 °C. Yield 93.1%. It contains 77.9% of N-(phosphonomethyl)-glycine.

Example I.20

360 g (2.13 moles) of N-(phosphonomethyl)-glycine are reacted at room temperature with 126 (2.13 moles) of isopropylamine in 100 ml of water. On keeping the mixture obtained below 100°C for 1 hour it is cooled back to room temperature and after standing for 2 hours the precipitate is filtered off. The product is hygroscopic. It is extracted twice by treatment with 200 ml of absolute ethanol each, filtered and dried. 476.0 g of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. Melting range 150 - 154°C, readily soluble in water, non-hygroscopic, Yield: 98%. Contains 74% N-(phosphonomethyl)-glycine.

Example I.21

The reaction is carried out as in Example I.20 with the difference, that the water is eliminated by evaporation and the remaining solid, hygroscopic salt is treated as indicated above.

485.6 g of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. Melting range 150 - 155°C, readily soluble in water, non-hygroscopic, Yield:99.9%. Contains 73.8% N-(phosphonomethyl)-glycine.

Example I.22

The reaction is carried out as in Example I.20 with the difference, that the aqueous solution obtained is dried by evaporation and the remaining solid, hygroscopic salt is treated as indicated above. The mono-isopropylammonium salt

WO 92/18513

of N-(phosphonomethyl)-glycine obtained shows the melting range 148 - 152°C, readily soluble in water, non-hygroscopic. Yield:99%. Contains 73.9% N-(phosphonomethyl)-glycine.

Example I.23

360 g (2.13 moles) of N-(phosphonomethyl)-glycine are reacted with 252 g of isopropylamine (4.3 moles) at room temperature in 100 ml of water. 360 g of N-(phosphonomethyl)-glycine are added and the reaction mixture is heated below 100°C for 1 hour. On cooling the precipitate is filtered. The hygroscopic product is extracted twice by treatment with 200 ml of absolute ethanol each, filtered and dried. 962 g of mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. Melting range 154 - 157°C, readily soluble in water, non-hygroscopic. Yield:99%. Contains 74% N-(phosphonomethyl)-glycine.

Example I.24

360 g of N-(phosphonomethyl)-glycine are reacted with 126 g of isopropyl amine at room temperature in 100 ml of water: After precipitating the product by addition of 500 ml of absolute ethanol, the precipitate is dried and ground to give 480 g of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine. Melting range 148 - 152°C, readily soluble in water, non-hygroscopic, Yield:99%. Contains 73.9 % N-(phosphonomethyl)-glycine.

Example I.25.

After performing the reaction as in Example I.24 and heating the aqueous reaction mixture at 100°C for 1 hour an oily mixture is obtained which is dried in an exsiccator containing phosphorus pentoxide or calcium chloride at room temperature for 24 hours. Thereafter it is extracted with 96% ethanol, filtered and dried to give 242.5 g of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine. Melting range 154 - 157°C, readily soluble in water, non-hygroscopic, Yield:99%. Contains 74% N-(phosphonomethyl)-glycine.

Example I.26.

The reaction is carried out as described in Example I.25. To the oily reaction mixture obtained 2 g of the di-isopropylammonium salt of N-(phosphonomethyl)-glycine are added which makes to precipitate the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine after stirring for 10 minutes. The white salt is filtered, extracted with 96% ethanol at room temperature, filtered and dried. 480 g of mono-isopropylammonium salt of N-(phosphonomethyl)-glycine are obtained. Melting range 147 - 152°C, readily soluble in water, non-hygroscopic, Yield:99%. Contains 73.6 g of N-(phosphonomethyl)-glycine.

II: FORMULATIONS

Example II.1.

A mixture of 0.5 g of ethoxylated nonyl-phenol and 2.84 of ethoxylated alkylamine additive material are dissolved in 40 ml of ethanol at room temperature. The solution is homogenized after addition of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine prepared according to Example I.2 and the ethanol is evaporated. 63.3 g of a product is obtained, which contains 69.6 % g of N-(phosphonomethyl)-glycine and is non-hygroscopic, readily soluble in water.

Example II.2

A slurry in 30 ml of ethanol is prepared from the auxiliary materials comprising 1.1 g of ethoxylated nonyl-phenol, 6.39 g of ethoxylated alkyl amine, 12.69 g of ethoxylated fatty amine and 9.28 g of fatty alcohol polyglycole ether, 60 g of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine prepared according to Example I.3 are added and the slurry is homogenized after addition of 4.4 g of urea. On evaporation of the ethanol 93 g of a product are obtained, containing 47.4% of N-(phosphonomethyl)-glycine, non-hygroscopic and readily soluble in water.

Example II.3.

A slurry in 30 ml of methanol is prepared from the auxiliary materials comprising 1.53 g of ethoxylated nonyl-phenol, 3.89 g of ethoxylated alkyl amine, 7.92 g of ethoxylated fatty amine and 5.97 g of iso-tridekanol polyglycole ether, 60 g of mono-isopropylammonium salt of N-(phosphonomethyl)-glycine prepared according to Example I.1 are added and the slurry is homogenized after addition of a mixture consisting of 2.78 g of potassium chloride, 0.03 g of 1-naphthyl acetic acid and 0.08 g of boric acid. On evaporation of the alcohol 82 g of a product are obtained, containing 53.8% of N-(phosphonomethyl)-glycine, non-hygroscopic and readily soluble in water.

Example II.4

35 g of N-(phosphonomethyl)-glycine mono-isopropylammonium salt prepared according to Example I.2 are homogenized with a solution of 40 g of auxiliary material Hyspray in 60 ml of ethanol. On evaporation of the alcohol 125 g of a product are obtained which is non-hygroscopic, readily soluble in water and contains 50.4 g of N-(phosphonomethyl)-glycine.

Example II.5

Using the method of Example I.11. with the difference that 10 g of lauropal-x auxiliary product are added to the slurry in surplus. A similar product as in Example 11 is obtained with the same yield.

Example II.6

Using the method of Example I.12. with the difference that also 50 g of ammonium hydrogen carbonate are added to the slurry, and 50 g of Hyspray are used instead of 30 g. Thus 195 g of a product are obtained which is non-hygroscopic, readily soluble in water, containing 32.3% of N-(phosphonomethyl)-glycine.

Example II.7.

Using the method of Example II.4. with the difference that 80 g of Hyspray and 10 g of lauropal-x are used in 100 ml ethanol with 85 of the mono-isopropylammonium salt of N-(phosphonomethyl)-glycine prepared according to Example I.2, while 70 g of ammonium hydrogen carbonate and 50 g of ammonium sulphate are added to the slurry.

295 g of a product are obtained which is non-hygroscopic, readily soluble in water, containing 21.3% of N-(phosphonomethyl)-glycine.

Example II.8.

Using the method of Example II.7. with the difference that the quantity of Hyspray auxiliary product is 50 g, 100 ml of ethanol, 50 g of ammonium hydrogen carbonate and 500 g of ammonium sulphate used. 695 g of a product are obtained which

WO 92/18513

PCT/HU92/00016

is non-hygroscopic, readily soluble in water, containing 9 % of N-(phosphonomethyl)-glycine.

Example II.9.

The auxiliary products 0.2g of ethoxylated nonyl-phenol and 1.2 g of ethoxylated alkylamine are dissolved in 10 ml of ethanol at room temperature. The solution is homogenized with 24g (0.1 mole) of mono-isopropylammoniumsalt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid, the ethanol is evaporated. 25.3g of a non-hygroscopic product are obtained, which is readily soluble in water containing 71% of the mono-isopropylammonium salt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid.

Example II.10.

The auxiliary products 0.2g of ethoxylated nonyl-phenol and 7,3 g of ethoxylated fatty acid are admixed with 5 ml of ethanol to give a slurry which is homogenized with 24g (0.1 mole) of the mono-isopropylammoniumsalt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid (prepared according to Example 17, and the ethanol is evaporated. 31.4g of a non-hygroscopic product are obtained, which is readily soluble in water and contains 57.6% of the mono-isopropylammoniumsalt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid.

Example II.11

0.2g of ethoxylated nonyl-phenol and 1,2 g of ethoxylated alkylamine are admixed with 8 ml of ethanol to give a slurry which is homogenized with 19.8g (0.1 mole) of the ammonium salt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid (prepared according to Example II.8 and the alcohol is evaporated. 21.1g of a non-hygroscopic product are obtained, which is readily soluble in water and contains 85% of the ammonium salt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid.

Example II.12

0.2g of ethoxylated nonyl-phenol, 1.2 g of ethoxylated alkyl

WO 92/18513

PCT/HU92/00016

amine and 6 g of ethoxylated fatty amine are admixed with 8 ml of ethanol to give a slurry which is homogenized with 20 g (0.1 mole) of the ammonium salt of (3-amino-3-carboxy-propyl)-methane-phosphinic acid (prepared according to Example I.11). On working as above 26.1 g of a similar product as above are obtained, containing 65% of (3-amino-3-carboxy-propyl)-methane-phosphinic acid - which in the following is abbreviated "acmpa".

Using the above methods the following compositions are prepared:

If desired the water-soluble and wettable or dispersible solid products may be subjected to fine grinding in a mill or other suitable grinding means.

Exam- ple	acmpa- salt	acmpa- content %	ethox. nonyl- phenol	auxiliary products % ethox. fatty amine	amm. sul- fate	poly- alkox. fatty alcohol
II.13	i.propyl	98	2			
II.14	i.propyl	84	1	15		
II.15	ammonium	98	2			
II.16	ammonium	80	2	18		
II.17	i.propyl	84	1	10	5	
II.18	ammonium	68	1	10	20	1

Example II.19

(3-amino-3-carboxy-propyl)- methane-phosphinic acid i.propylamine salt	33%
N-(phosphonomethyl)-glycine i.propylamine salt	65%
ethoxylated nonylphenol	1%
polyalcoxylated fatty alcohol	1%

Example II.20

(3-amino-3-carboxy-propyl)- methane-phosphinic acid ammonium salt	33%
--	-----

N-(phosphonomethyl)-glycine ammonium salt

65%

ethoxylated nonylphenol

1%

polyalcoxylated fatty alcohol

1%

Example II.21

(3-amino-3-carboxy-propyl)-

methane-phosphinic acid i.propylamine salt

26%

N-(phosphonomethyl)-glycine i.propylamine salt

53%

ethoxylated nonylphenol

1%

ammonium sulfate

20%

Example II.22

(3-amino-3-carboxy-propyl)-

methane-phosphinic acid ammonium salt

26%

N-(phosphonomethyl)-glycine ammonium salt

53%

ethoxylated nonylphenol

1%

ammonium sulfate

20%

Example II.23

(3-amino-3-carboxy-propyl)-

methane-phosphinic acid i.propylamine salt

55%

ethoxylated fatty amine

18%

imazapryl-i.propylamine

27%

Example II.24

(3-amino-3-carboxy-propyl)-

methane-phosphinic acid ammonium salt

55%

ethoxylated alkyl phenol

27%

imazapryl-ammonium

27%

Example II.25

(3-amino-3-carboxy-propyl)-

methane-phosphinic acid ammonium salt

54%

ethoxylated fatty amine

19%

imazapryl-ammonium

27%

WO 92/18513

PCT/HU92/00016

Example II.26

(3-amino-3-carboxy-propyl)-	
methane-phosphinic acid i.propylamine salt	32%
ethoxylated alkyl amine	4%
2,2-D-i.propylamine salt ?	64%
ethoxylated nonyl phenol	1%

Example II.27

(3-amino-3-carboxy-propyl)-	
methane-phosphinic acid i.propylamine salt	30%
polyalkoxylated fatty alcohol	20%
Triazine	30%
silicium dioxyde	5%
ammonium sulphate	15%

Example II.28

(3-amino-3-carboxy-propyl)-	
methane-phosphinic acid ammonium salt	30%
polyoxylated fatty alcohol	15%
Triazine	30%
ammonium sulphate	25%

Example II.29

(3-amino-3-carboxy-propyl)-	
methane-phosphinic ammonium salt	68%
Oxyfluorophen	14%
ethoxylated nonyl-phenol	1%
polyoxyethylated fatty acid	5%
ammonium sulphate	5%
silicium dioxyde	5%

Example II.30

1 kg of the compositions prepared according to the Examples above are filled into a bag the size of which is suitable to take the quantity. The bag is made of poly-(vinyl-alcohol), which is plastified with a polyvalent alcohol. The bag is square shaped and is closed on its three sides. The

properties of the powders according to the examples as above are such that it is easy to fill the same into the bags. The bags are then closed by welding.

When using the above bags - after storing and transferring the same to the place of use - they are thrown into the needed amount of water while stirring intensely. The polymer disappears within 2 minutes while the herbicide composition is dissolved completely or is dispersed in the water to give a composition which can be used directly in the field.

In the following Examples different water- soluble or water- wettable solid compositions are enumerated. The active ingredient non-hygroscopic mono-isopropylammonium salt of N-(phosphonomethyl)-glycine is always abbreviated "solid glyphosate mono - ipa-salt".

Example II.31

Solid glyphosate mono-ipa-salt	98%
Ethoxylated nony-phenol	2%

Example II.32

Solid glyphosate mono-ipa-salt	95%
Ethoxylated-nonyl-phenol	1%
Ethoxylated alkylamine	4%

Example II.33

Solid glyphosate mono-ipa-salt	80%
Ethoxylated-nonyl-phenol	2%
Ethoxylated fatty amine	18%

Example II.34

Solid glyphosate mono-ipa-salt	77%
Ethoxylated-nonyl-phenol	1%
Ethoxylated alkylamine	7%
Ethoxylated fatty amine	10%
Urea	5%

Example II.35

Solid glyphosate mono-ipa-salt	60%
Ethoxylated-nonyl-phenol	1%
Ethoxylated alkylamine	7%
Ethoxylated fatty amine	10%
Polyalkoxylated fatty alcohol	2%
Ammonium-sulphate	20%

Example II.36

Solid glyphosate mono-ipa-salt	70%
Ethoxylated-nonyl-phenol	1%
Ethoxylated alkylamine	4%
Ammonium-sulphate	20%
Silicium dioxide	5%

Example II.37

Solid glyphosate mono-ipa-salt	68.00%
Ethoxylated-nonyl-phenol	2.00%
Ethoxylated-alkylamine	4.50%
Ethoxylated fatty amine	9.60%
Isotridecyl alcohol-polyglycolether	7.30%
KCl	3.45%
1-naphthyl acetic acid	0.05%
Boric acid	0.10%

Example II.38

Solid glyphosate mono-ipa-salt	50%
Isopropylammonium salt of 2,4-D	32%
Ethoxylated-nonyl-phenol	1%
Ethoxylated-alkylamine	4%
Ammonium-sulphate	8%
Silicium dioxide	5%

Example II.39

Solid glyphosate mono-ipa-salt	40%
Glufosinate mono-ipa-salt	7%
Ethoxylated-nonyl-phenol	2%

WO 92/18513

PCT/HU92/00016

Sodium-lignine sulphonate	3%
Ammonium-sulphate	33%
Silicium dioxyde	5%
Caoline	10%

Example II.40

Solid glyphosate mono-ipa-salt	40%
Dimethipine	7%
Ethoxylated-nonyl-phenol	2%
Sodium-lignine sulphonate	3%
Ammonium-sulphate	33%
Silicium dioxyde	5%
Caoline	10%

Example II.41

Solid glyphosate mono-ipa-salt	50%
Oxyfluorphen	4%
Ethoxilated-nonyl-phenol	2%
Sodium-lignine sulphonate	3%
Silicium dioxyde	16%
Caoline	20%

Example II.42

Solid glyphosate mono-ipa-salt	40%
Ethoxylated-nonyl-phenol	1%
Ethoxylated alkylamine	4%
Ethoxylated fatty amine	15%
Ammonium-sulphate	30%
Caoline	10%

Example II.43

Solid glyphosate mono-ipa-salt	80%
ATPLUS 411	19%
Polyalkoxylated fatty alcohol	1%

Example II.44

Solid glyphosate mono-ipa-salt	40%
Glufosinate ammonium salt	20%

WO 92/18513

PCT/HU92/00016

Ethoxylated nonyl-phenol	1%
Ethoxylated alkylamine	4%
Ammonium-sulphate	35%

Example II.45

Solid glyphosate mono-ipa-salt	0.05%
Ammonium-sulphate	80.00%
Ethoxylated nonyl-phenol	1.00%
Ethoxylated fatty amine	18.95%

Example II.46

Solid glyphosate mono-ipa-salt	99%
Ethoxylated nonyl-phenol	1%

Example II.47

Solid glyphosate mono-ipa-salt	1%
Dissovet S	99%

Example II.48

Solid glyphosate mono-ipa-salt	1%
Ammonium-sulphate	70%
Ammonium-nitrate	28%
Polyalkoylated fatty alcohol	1%

Example II.49

Solid glyphosate mono-ipa-salt	99.9%
Polyalkoxylated fatty alcohol	0.1%

Example II.50

68g of mono-isopropylammonium salt of N-(phosphonomethyl)-glycine, 3 g of 3,6-dichloro-2-pyridine-2-carbonic acid, 10 g of lignine sulphonic acid potassium salt, 1 g of oleyl-methyl-tauric acid sodium salt, 4g of polyoxylated nonylphenol, 4 g of polyethane-alkylamide and 10 g of synthetic silicium dioxyde are ground to 7 - 15 micron size. A wettable powder is obtained which contains 50% of N-(phosphonomethyl)-glycine and 17.5% of metribazine, which can be used in the known manner.

Example II.51

68 g of mono-isopropylammonium salt of N-(phosphonomethyl)-glycine, 10 g of 2,3-dihydro-5,6-dimethyl-1,4-lithium--1,1,4,4-tetroxyde, 3 g of polyethoxylated nonylphenol, 7 g of polyethoxylated fatty acid amine, 7 g of lignine - sulphonic acid potassium salt and 5 g of synthetic silicium dioxide are ground to the desired size to give a non-hygroscopic product for agricultural use.

Example II.52

68 g of mono-isopropylammonium salt of N-(phosphonomethyl)-glycine, 8.75 g of 4-amino-3-methylmercapto- 6- terc.butyl-1,2,4- triazine, 5 g of lignine-sulphonic acid potassium salt, 5 g of polyethoxylated nonyl-phenol, 1 g of oleyl-methyltauric acid sodium salt and 12.25 g of Aerosil are ground to 7 - 15 micron size. The powder obtained is non-hygroscopic, N-(phosphonomethyl)-glycine content: 50%. It can be used for suspension formulations to be used in agriculture.

III. ANALYTICAL TESTS

III.1. FREE FLOW TESTS

When making formulations for use in the water-soluble bags according to our invention it is necessary to subject the products to the free-flow test in order to clarify whether or not they are suitable for this purpose.

100 of the non-hygroscopic salts according to the invention are filled into a funnel having a 2 cm width opening off-take and the period of time is determined which is needed for the product to flow out. For free-flowing powders or such that are considered to have good flowing properties, this has to happen within 10 seconds. Table I shows some results obtained with some products according to our invention

Table I.

Example	Flowing time (sec)
II.31	4.0
II.32	2.0
II.33	4.0
II.34	2.0
II.35	1.5
II.36	2.0
II.37	7.0
II.38	5.0
II.39	5.0
II.40	9.5
II.41	7.2
II.42	4.5
II.43	4.0
II.44	3.0
II.12	5.0
II.13	5.0

III.2 X-RAY DIFFRACTION TESTS

The following samples of different mono-isopropylammonium salts of N-(phosphonomethyl)-glycine were subjected to examination, prepared substantially according to the Examples as indicated:

TABLE II

Example	solvent used	crystal type found
I.12	abs. ethanol	α
I.1	96% ethanol	α
I.13	water	β
-	methanol/diethyl ether*	β

*freshly prepared

Method: The tests were performed using an X-ray diffractometer of the HZG-4/C type. Source of irradiation: $\text{CoK}\alpha$ $\lambda = 1.79 \text{ \AA}$ (Co tube 30 keV 12 mA° Fe filter). Goniometer sensor velocity $1^\circ/\text{minute}$. The sample holder was made of Al.

The method of preparing the samples and testing were always the same. On the basis of the X-ray-grams the d lattice level values were calculated and their relative intensities were given as indicated in Table III. Some of the X-ray-grams are also shown as Figures 4 and 5.

It is clear from the results that the samples show two different structures which we designated crystal types α and β respectively as indicated in Table II.

TABLE III

abs. ethanol		96% ethanol		methanol-diethyl- ether		water	
dA°	I/I_0	dA°	I/I_0	dA°	I/I_0	dA°	I/I_0
11.0	100	11.0	100	7.03	100	7.00	100
9.06	47	9.09	45	4.83	16	4.83	13
7.41	13	7.39	14	4.56	19	4.54	29
5.94	42	5.95	43	4.48	46	4.47	43
5.54	38	5.56	46	4.27	23	4.26	29
		5.38	9	4.17	46	4.17	33
4.98	12	5.0	15	4.06	37	4.05	40
4.85	33	4.86	37	3.937	48	3.937	49
4.55	9	4.56	10	3.831	85	3.820	76
		4.37	11	3.621	6	3.62	7
4.298	9	4.30	9	3.527	55	3.515	48
4.13	83	4.13	94	3.358	21	3.351	20
		4.08	31	3.297	18	3.30	19
4.01	58	4.01	48	3.198	10	3.195	9
3.82	14	3.83	15	3.140	39	3.136	34
3.782	15	3.79	12	2.917	37	2.912	28
3.710	51	3.71	56	2.821	4	2.815	6
		3.59	6	2.739	11	2.737	8
3.48	10	3.488	11	2.654	6	2.650	6
3.403	29	3.403	24	2.547	7	2.545	10
3.295	9	3.293	9	2.502	6	2.502	8
3.257	17	3.259	16	2.421	12	2.420	18

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3,189	29	3,191	34	2,35	21	2,405	11
3,035	7	3,037	6			2,34	15
2,985	6	2,983	6				
2,929	7	2,932	7				
		2,909	6				
2,790	10	2,789	10				
		2,688					
2,502	18	2,502	24				

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III.3. SOLUBILITY TESTS

III.31.

Table IV illustrates some solubility values of the mono-isopropylammonium salts and di-isopropylammonium salts of N-(phosphonomethyl)-glycine on the basis of which the processes according to our invention can be reduced to practice. All solvents or solvent-mixtures can be used for our processes which show a reasonable solubility - difference between the salts and products that have to be separated.

TABLE IV
SOLUBILITY g/liter

solvent	mono-IPA* salt	di-IPA* salt	glyphosate**
water	1470	1980	12
methanol	56	570	< 0.3
ethanol			0.2
n-propanol	0.7	170	< 0.5
i-propanol			< 0.5
n-butanol	0.1	35	
benzyl-alcohol	0.5	420	< 0.2
propylene-glycol	184.0	244	< 0.
dimethyl-formamide	1.8	22	< 0.2
benzene	< 0.1	< 0.1	< 0.1
i.propyl amine	< 0.1	< 0.1	

*= iso-propyl amine

**= N-(phosphonomethyl)-glycine

Example III.32

The values given below can be used to evaluate the best solvents to be used in the case of (3-amino-3-carboxy-propyl)-methane phosphinic acid.

TABLE V.
SOLUBILITY g/liter (25°C)

solvent	mono-ammonium	mono-ipa-salt	glufosinate
	salt		
water	2000	1150	99
methanol	14	260	23
ethanol	4	5	9
n-propanol	6	5	9
i-propanol	10	4	12
benzylalcohol	9	300	9
propylene-glycole	9	280	21
dimethyl formamide	10	8	12
benzene	-	-	7

III. UPTAKE OF HUMIDITY

III.1.

The samples were investigated in open containers, at 60% humidity and 25°C. The results are shown in Table VI.

salt	days					
	1	2	7	14	30	90
<hr/>						
mono-isopropyl-						
ammonium salt of						
N-(phosphonomethyl)						
-glycine*	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
di-isopropyl-						
ammonium salt of						
N-(phosphonomethyl)						
-glycine**	13.0%	14.5%	16.1%	18.8%	19.2%	30.9%
<hr/>						

Appearance:

* the mono-isopropylammonium salt was unchanged after 30 days.

* the di-isopropylammonium salt was sticky and hygroscopic within 1 day and was completely liquid within 14 days.

IV. BIOLOGICAL EXAMPLES

IV.1.

Compositions formulated according to Examples II.34 or II.36 are dispersed in water to give 3g active ingredient / liter liquids. 6mg of the active ingredient of each sample were sprayed on 15 day old barley plants, kept in vessels under green house conditions. On the 4th day the chlorophyll quantity falling on unit quantities of dry substance in the plants was determined. The results are shown in Table VII

Table VII

Control	9.26 mg/g
Example II.9	3.42 mg/g
Example II.11	3.43 mg/g

Growth depression was determined as well. The results are shown in Table VIII.

Table VIII

Control	0
Example II.9	8.75 cm
Example II.11	8.5 cm

IV.2.

According to the methods of Example V.1. 15 day old bean plants were sprayed with 4.5mg of active ingredient/vessel (1.5ml of the liquid) and the photosynthetic activity was determined on the third day. The results are summarized on Table IX.

Table IX

	Control	Example II.9	Example II.11
F	685	340	325
F	556	89	116
	0.517	0.062	0.134
	2.402	0.404	0.929

CLAIMS

1.

Process for the preparation of mono-ammonium-salts of the general formula (I), where

-R¹ stands for hydroxy or alkyl,

-A stands for 1-4 alkyl-amino- or amino-alkyl-groups containing primary or secondary amino-groups, preferably -CH₂-NH- or -CH(NH₂)-CH₂- groups,

- B stands for ammonium-ion, or alkyl - substituted ammonium-ion-

characterized by synthesizing of a solid, non-hygroscopic salt by preparing the mono-ammonium-salt of general formula (I), according to any method known generally for the preparation of salts, whereby - along with avoiding other contaminations - on the course of or after salt-formation the di-ammonium-salt of the general formula (V), where

-R¹, A and B stand for the above -

is eliminated or its formation is repressed.

2.

Process for the preparation of mono-ammonium-salts of the general formula (I), where

-R¹, A and B stand for the above -

characterized by the use of the following processes alone or in combination with each other

a.)

reacting the acid of the general formula (II)

- R¹ and A have the meaning as above -

with a reactant of basic (alkaline) character capable to form the ion B⁺ -

- B has the meaning as above -

in an organic, polar solvent or in solvent- mixture containing an organic, polar solvent, in which the salt and acid of general formulae (I) and (II) where

-R¹, A and B stand for the above -

are not, or only slightly soluble, while the reactant of

basic character and the di-ammonium-salt of general formula (V) where

-R¹, A and B stand for the above -

formed as by-product are readily soluble, and optionally the reaction mixture is heated subsequently or

b.)

a di-ammonium-salt of the general formula (V), where

-R¹, A and B stand for the above -

is reacted with an acid of the general formula (II) where

-R¹, A and B stand for the above -

under the reaction conditions of the method a) or

c.)

an acid of the general formula (II) where

-R¹ and A stand for the above -

is reacted with a salt capable to form the ion B⁺

- B stands for the above -

under the reaction conditions of the method a) or

d.)

a hygroscopic salt of the general formula (I) where

-R¹, A and B stand for the above -

is extracted with an organic, preferably polar solvent or a solvent-mixture containing an organic, polar solvent, in which the mono-ammonium salt of general formula (I) where

-R¹, A and B stand for the above -

is insoluble or slightly soluble, while the di-ammonium-salt of general formula (V) where

-R¹, A and B stand for the above -

is readily soluble or

e.)

eliminating at room temperature in vacuo or with heating from a di-ammonium salt of general formula (V) where

-R¹, A and B stand for the above -

or from a mono-ammonium salt which is contaminated with such di-ammonium-salt the quantity of the amine containing the B⁺-ion

- B stands for the above-
which is above the mole-equivalent or

f.)

reacting a salt of the acid of the general formula (II), where
-R¹, A and B stand for the above -
using the reaction conditions of the a.) method with a
reactant which is capable to form the ion B⁺ -
where B stands for the above,
and optionally isolating the salt of general formula (I) thus
formed -where
-R¹, A and B stand for the above -
preferably by filtration.

3.

Process according to any of claims 1 and 2 characterized
by using as a starting acid N-(phosphonomethyl)-glycine
of formula (III).

4.

Process according to any of claims 1 and 2, characterized
by using as the starting acid (3-amino-3-carboxy-
propyl)-methane-phosphinic acid of the formula (IV).

5.

Process according to any of claims 1 to 4, characterized
by using as solvents aliphatic alcohols contain-
ing 1-6 carbon atoms and/or poly-alcohols and/or aromatic al-
cohols containing 1-6 alkyl side chains.

6.

Process according to claim 5, characterized by
preparing the N-(phosphonomethyl)-glycine - mono-isopropyl-
ammonium-salt or - mono-ammonium-salt in the presence of etha-
nol and/or propanol.

7.

A process according to the method c.) of claim 1, character-

-45-

t e r i z e d b y reacting the acid of general formula (II)

- A and R¹ stand as above -

with the salt formed with a 1 or 2 basic carboxylic acid of the general formula (VI) - where

- R² stands for hydrogen, hydroxyl-, optionally substituted 1-4 alkyl-groups, optionally substituted aryl-group of the pK-values of the range 2,27 to 5,58.

8.

A process according to the method c.) of claim 1, c h a r a c -
t e r i z e d b y applying the trialkyl-ammonium salt of the
acid of the general formula (VI)

- R² stands as above -

which is added to the reaction in solid form or in solution

9.

A process according to claim 8 c h a r a c t e r i z e d b y
performing the reaction at 0 - 150 C°, preferably 20 - 80C°.

10.

A process according to claim 2, c h a r a c t e r i z e d b y
preparing mono-isopropylammonium salt of N-(phosphonomethyl)-
glycine with the pure α crystal type, melting at 158 - 163°C
by reacting N-(phosphonomethyl)-glycine and using the a.)
method.

11.

Solid, non-hygroscopic mono-ammonium salts of general formula (I) -where

-R¹, A and B stand for the above -

which are substantially free of diammonium-salts of the general formula (V)-where

-R¹, A and B stand for the above.

12.

Solid, non-hygroscopic mono-isopropylammonium salt of N-(phosphonomethyl)-glycine according to claim 11, of the α crystal type, having a melting range of 158 - 163 C° and the characteristic values of crystal - lattice - levels when measured by way of X-ray-diffraction are as follows: 11.0, 9.06, 5.94, 5.54, 4.13, 3.71 Å while the characteristic absorption bands obtained by FT-IR-spectroscopy are 1660, 1600, 1553, 1545, 1075, 513 and 475 cm⁻¹.

13.

Solid, non-hygroscopic, crystalline mono-isopropylammonium salts of N-(phosphonomethyl)-glycine according to claim 11, of the β crystal type, having a melting point range of 143 to 155 °C and the characteristic crystal - lattice - values when measured by way of X-ray-diffraction are as follows: 7.00, 4.83, 4.47, 3.35, 2.815, while the characteristic absorption bands obtained by FT-IR-spectroscopy are 1645, 1594, 1561, 1541, 1066, 500 and 455 cm⁻¹.

14.

Solid, non-hygroscopic, crystalline (3-amino-3-carboxypropyl)-methane-phosphinic acid mono-isopropylammonium salts according to claim 11, having a melting range of 199 - 203°C, while the characteristic absorption bands obtained by FT-IR-spectroscopy are 1640, 1601, 1530, 1138, 1037, 750 and 471 cm⁻¹.

15.

A herbicidal or plant-growth-regulating composition characterized by containing as an active ingredient an effective amount of the crystalline, non-hygroscopic salts of the general formula (I), where - R¹, A and B are as above.

16.

A herbicidal or plant-growth-regulating composition characterized by containing as an active ingredient an effective amount of a crystalline, non-hygroscopic (3-amino-3-carboxy-propyl)-methane-phosphinic acid mono-isopropyl ammonium salt.

17.

A herbicidal or plant-growth-regulating composition characterized by containing as an active ingredient an effective amount of the crystalline, non-hygroscopic N-(phosphonomethyl)-glycine mono-isopropylammonium salts of the α or β crystal type.

18.

A herbicidal or plant-growth-regulating composition according any of claims 14 to 16 characterized by containing as an active ingredient 0.1 to 99.9% of the above salts along with additive and auxiliary products which are used in pesticide industry and/or products which favorably modify the properties of the product for agricultural use.

19.

A herbicidal or plant-growth-regulating composition according to any of claims 15 to 18 characterized by containing as further ingredients such products which are as such pesticide ingredients per se.

20.

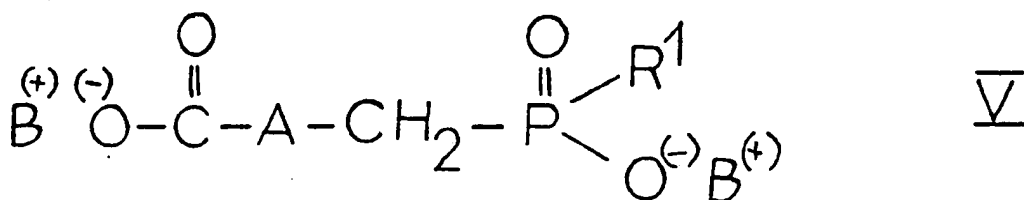
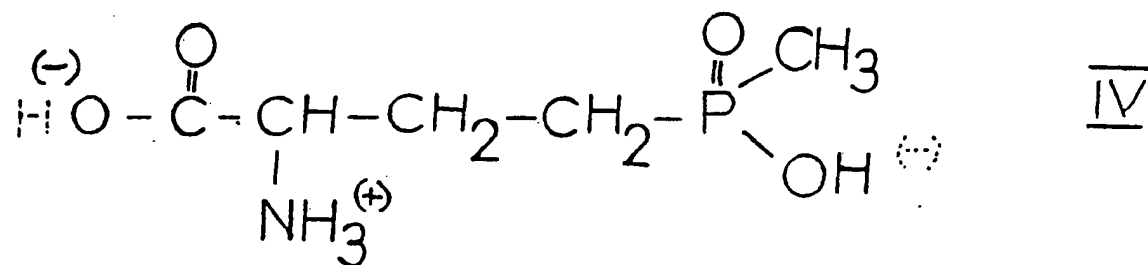
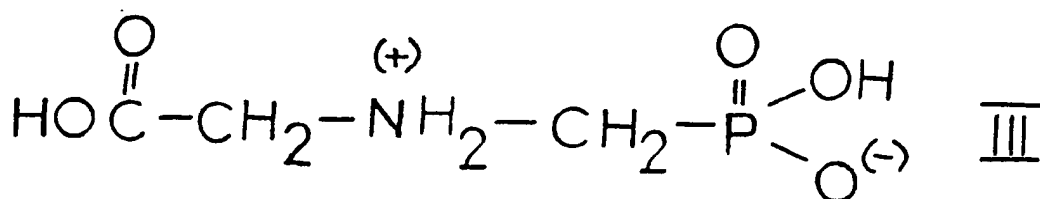
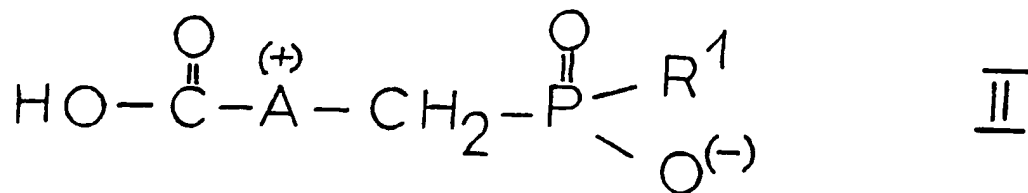
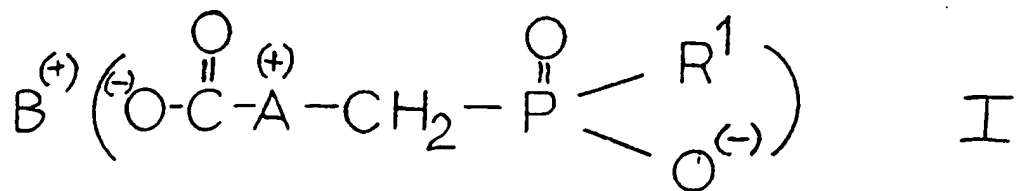
A process for the preparation of a herbicidal or plant-growth-regulating composition according to any of claims 15 to 19 characterized by formulating with the methods known for formulating of pesticides 0.1 to 99.9% of an active ingredient as claimed above together with auxiliary products used in pesticide formulation and/or with products which favorably modify the properties of the active ingredients when used.

21.

A herbicidal or plant-growth-regulating composition according any of claims 15 to 20 characterized by consisting of a bag, which is solid and preferably flexible in its dry state, which is made of a water-soluble polymer and which contains the compositions according to any of claims 15 to 20.

22.

A method to kill unwanted plants or weeds or to influence the growth of plants characterized by treating said plants in the field with an effective amount of a herbicidal or plant-growth-regulating composition according to any of claims 15 to 21 by way of dispersing the composition on the plants in the form of aqueous or water / organic solvent solutions or dispersions or suspensions.



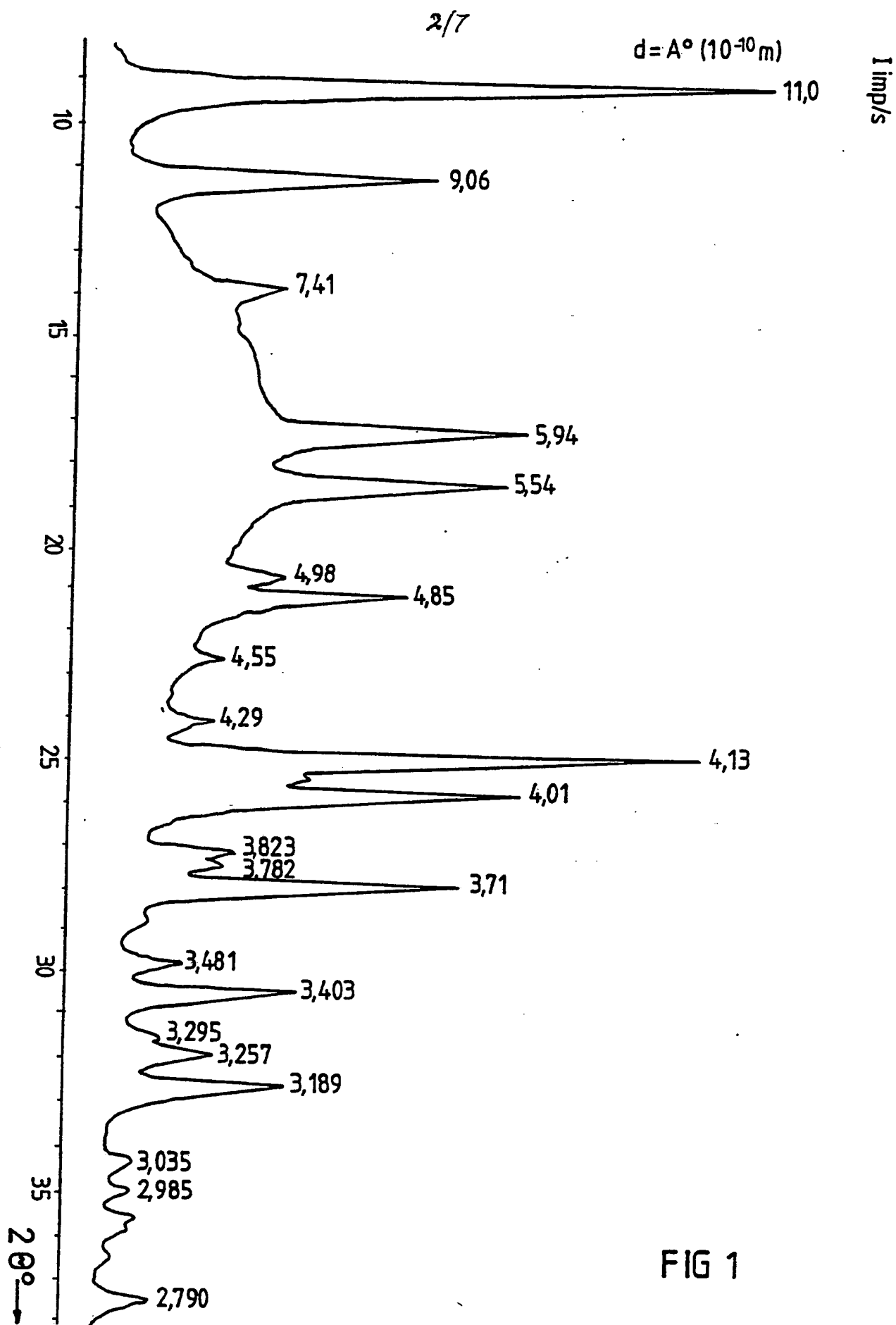
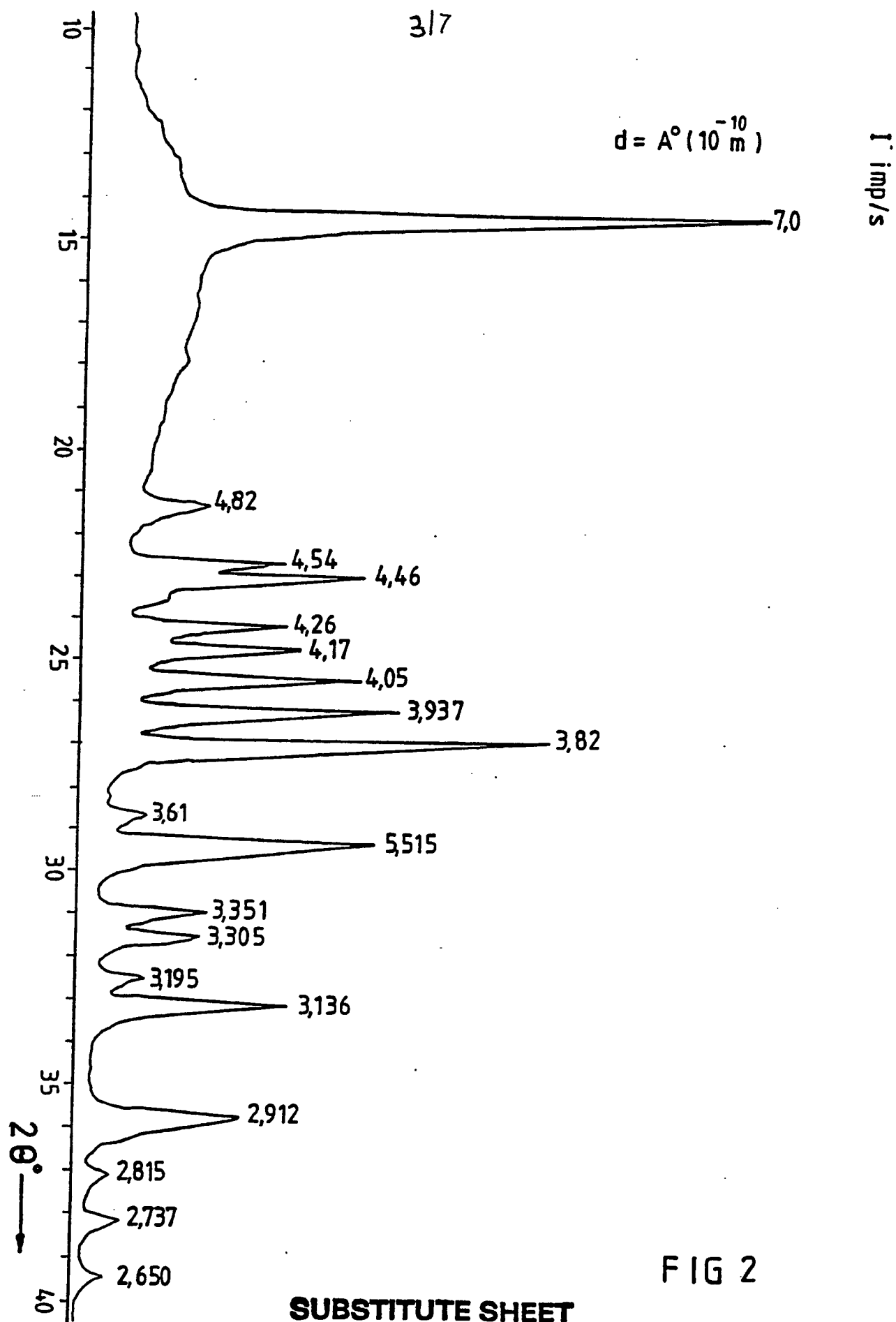


FIG 1

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4/7

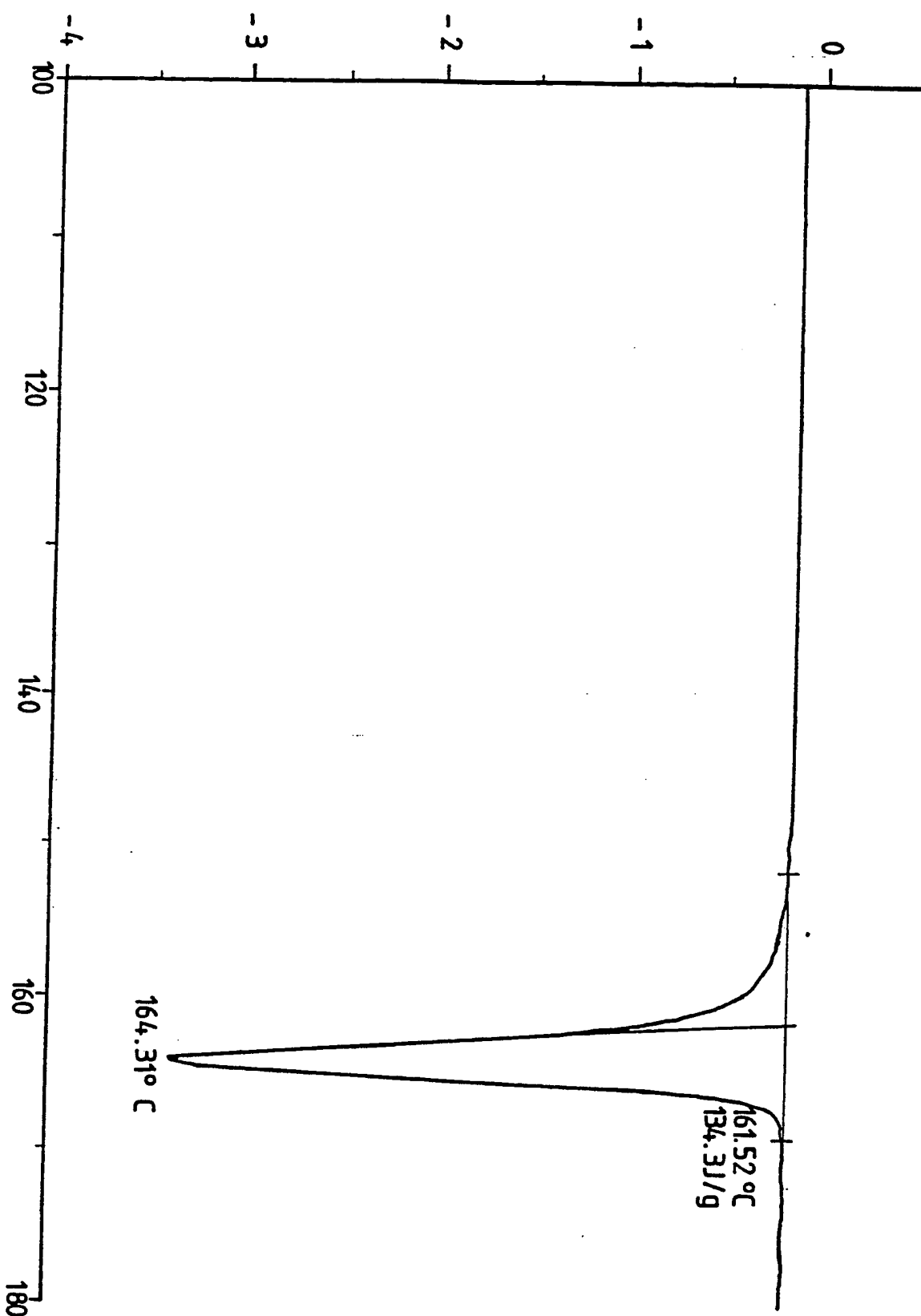


FIG 3

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5/7

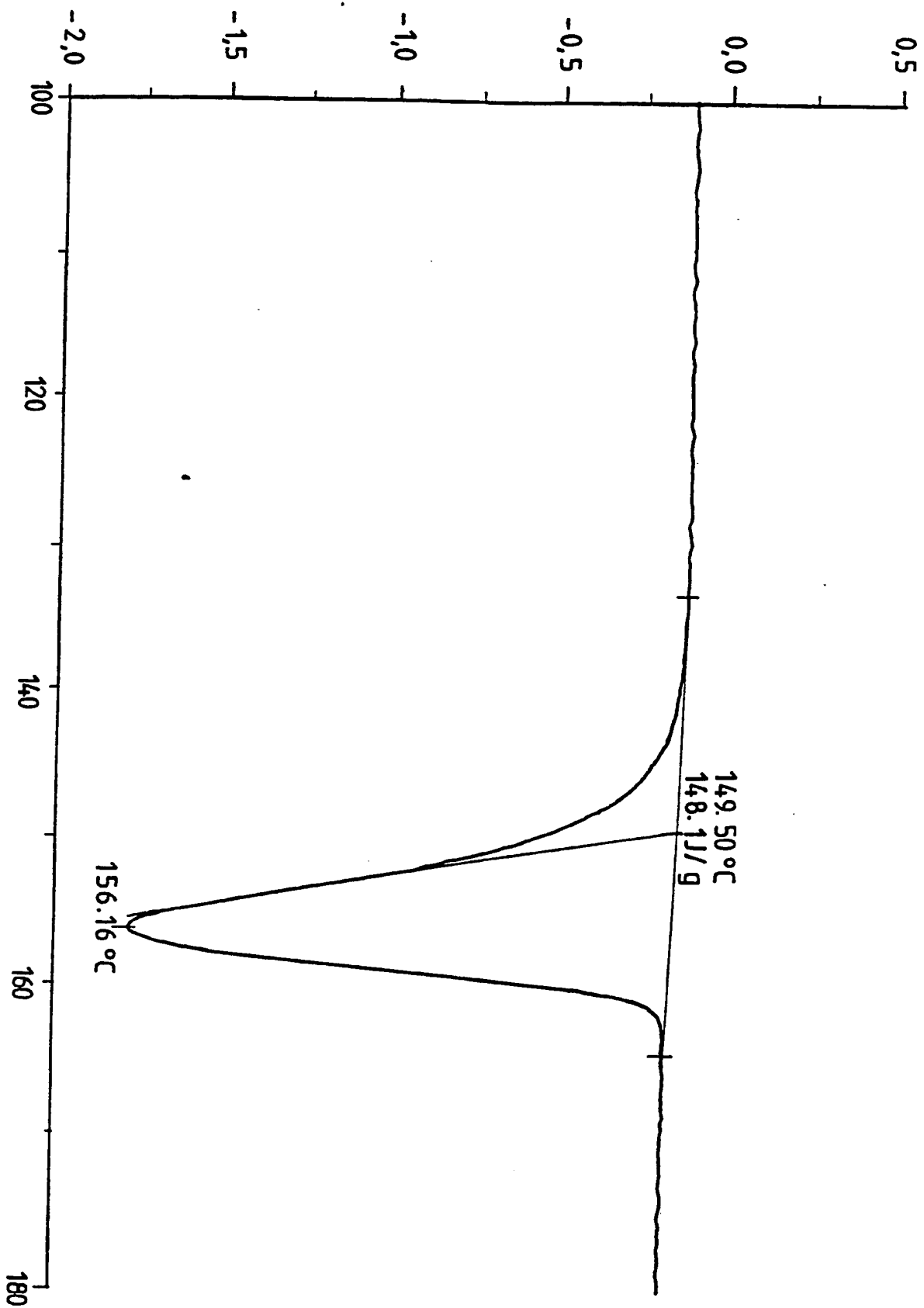
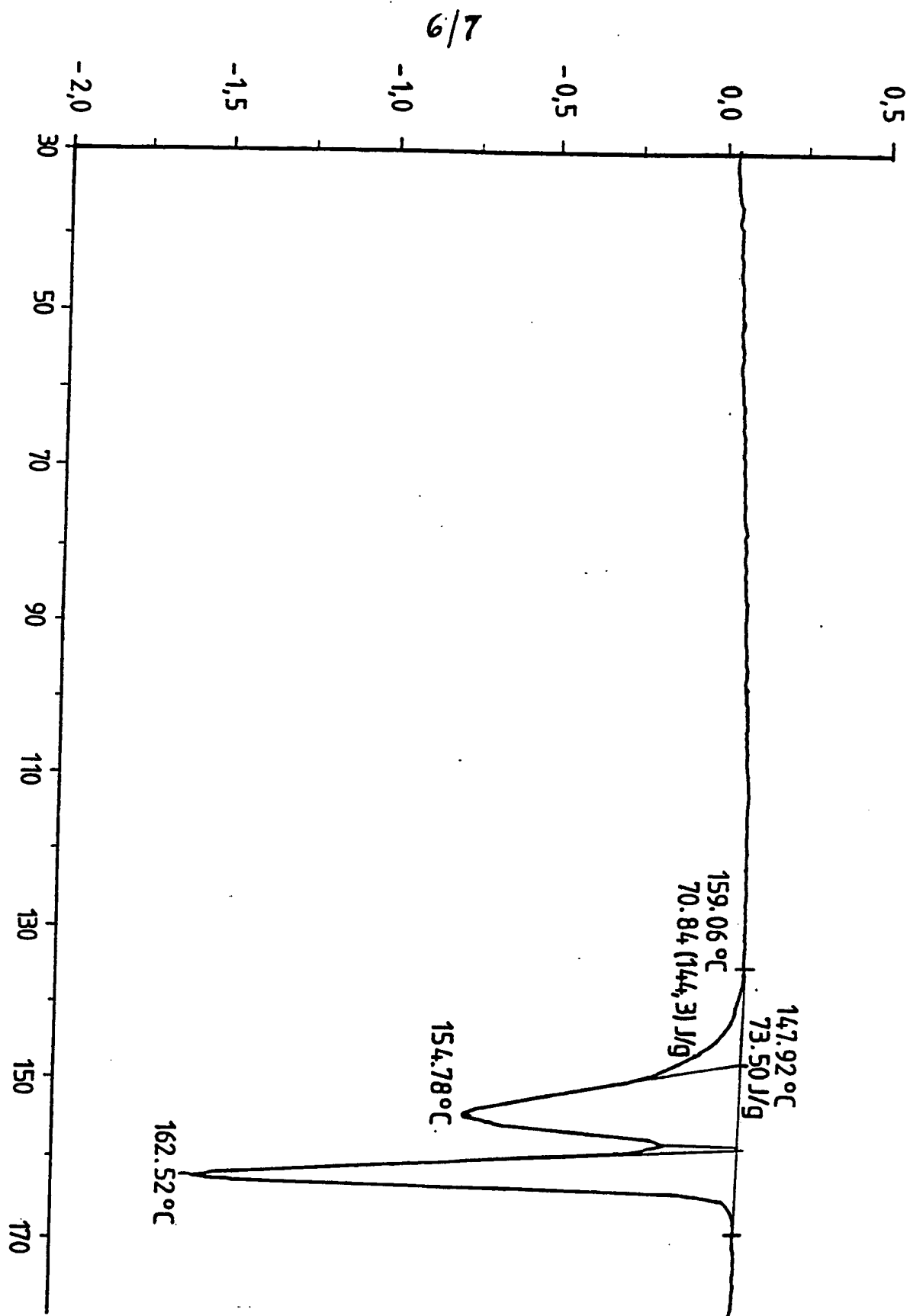


FIG 4



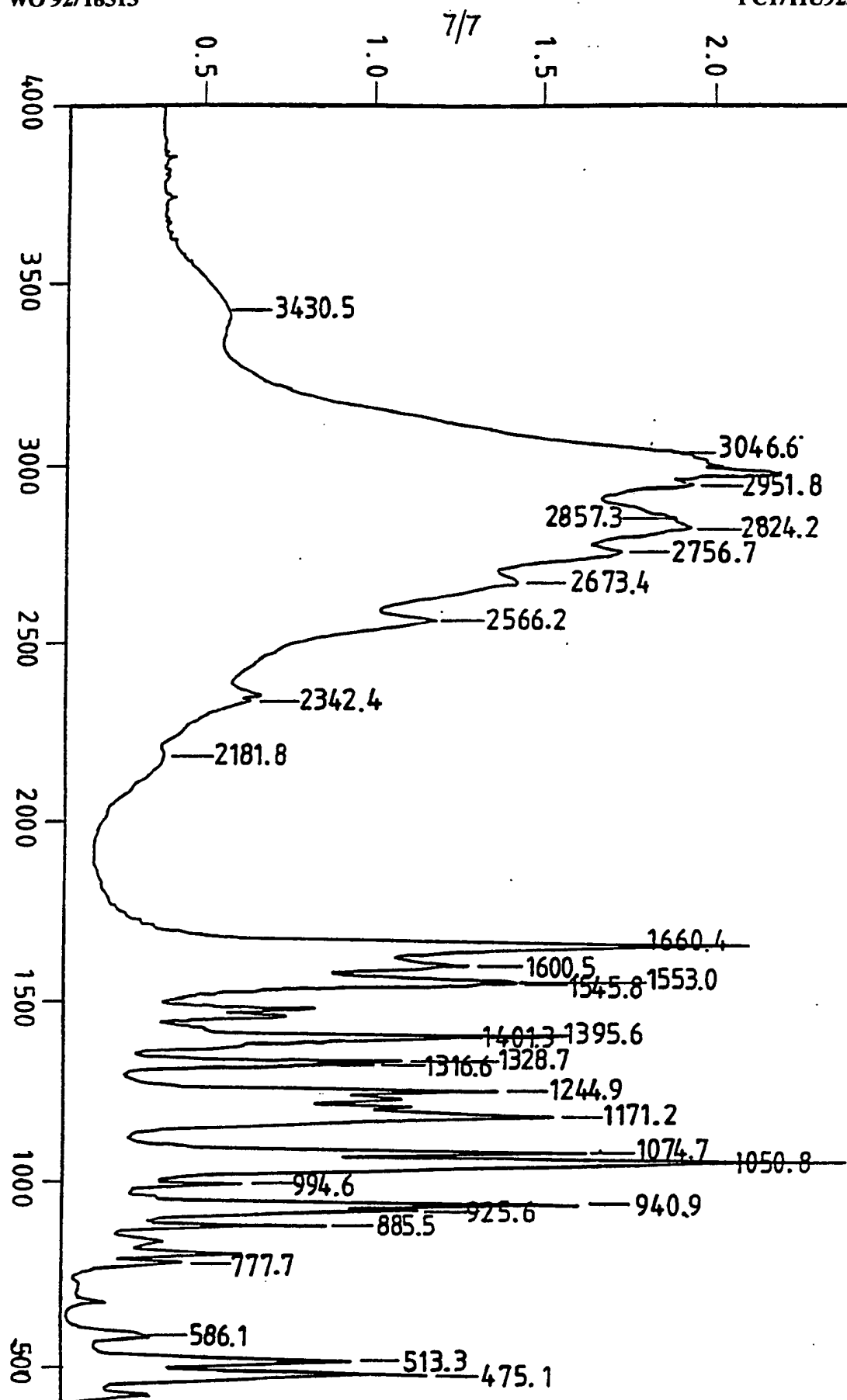
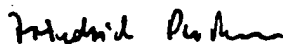


FIG 6

INTERNATIONAL SEARCH REPORT

International Application No PCT/HU 92/00016

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. ⁵ : C 07 F 9/38, 9/30; A 01 N 57/20		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int. Cl. ⁵ :	C 07 F 9/38, 9/40, 9/30, 9/32; A 01 N 57/20, 57/18	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
Chemical Abstracts (online STN)		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	Chemical Abstracts (online STN) Accession NO CA 106:45723m, R. Sales Barquets "((Carboxymethyl) amino)methanephosphonic acid salts with amines", see abstract, & ES, A1, 530 743.	1,15
A	EP, B1, 0 206 537 (STAUFFER), 20 September 1989 (20.09.89), see claims 1,7.	1,15,22
A	EP, A2, 0 256 608 (STAUFFER), 24 February 1988 (24.02.88), see claim 1.	1,15
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
02 June 1992 (02.06.92)	10 June 1992 (10.06.92)	
International Searching Authority	Signature of Authorized Officer	
AUSTRIAN PATENT OFFICE		

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/HU92/00016

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentedokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
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